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**PMR POLYIMIDES WITH IMPROVED
HIGH TEMPERATURE PERFORMANCE**

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ABSTRACT

Studies were performed to investigate the effect of substituting a hexafluoroisopropylidene connecting group for a carbonyl group of a PMR polyimide monomeric reactant on the thermo-mechanical properties and processability of graphite fiber reinforced PMR polyimide composites. Composites were fabricated utilizing PMR methodology. Monomeric reactant solutions of various stoichiometric ratios were used to impregnate Hercules HTS graphite fiber. The processing characteristics and elevated temperature (600° F) mechanical properties of the composites are described.

INTRODUCTION

PMR (in situ polymerization of monomer reactants on the surface of the reinforcing fibers) polyimide resins are beginning to achieve acceptance by fabricators for reasons of processability such as ease of prepregging, prepreg handleability, and the use of a low boiling solvent (methanol) as well as mechanical properties retention. The useful life of presently available PMR polyimide resins reinforced with high strength low modulus graphite fiber appears to be limited to approximately 600 hours at 600° F (ref. 1). The useful life of high modulus low strength graphite fiber/PMR polyimide composites appears to be greater than 1000 hours at 600° F (ref. 2).

Studies reported in reference 3 showed that by using the PMR approach it was possible to "tailor make" PMR polyimide matrix resins having desirable resin flow characteristics and excellent mechanical properties retention at temperatures up to 550° F (substantially greater than those observed at 600° F).

Currently available PMR polyimide resins are based on the monomeric reactants 5-norbornene-2,3-dicarboxylic acid monomethyl ester (NE), dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), and 4,4'-methylenedianiline (MDA). A reactant which offers considerable potential for improving the thermo-oxidative stability of PMR polyimide resins is the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis (phthalic acid) (HFDE). HFDE contains a hexafluoroisopropylidene connecting group which is more resistive to oxidation than the carbonyl linking group in BTDE. The parent compound of HFDE, 4,4'-(hexafluoroisopropylidene)-bis (phthalic acid), (HFA), is one of the constituents of Dupont's NR 150 condensation resins. The NR 150 resins exhibit improved thermo-oxidative stability compared to condensation polyimides containing carbonyl groups (ref. 4). However, the NR 150 resins require long cure schedules and final processing at temperatures above the glass transition temperature (T_g equals 650° - 800° F).

The purpose of this study is to investigate the effects of substituting HFDE for BTDE on thermo-oxidative stability of PMR polyimide matrix resins used to fabricate graphite fiber composites. This report describes the effects of this substitution on thermo-mechanical properties and processability of graphite fiber reinforced PMR polyimide composites.

Composites were fabricated from Hercules HTS graphite fiber and polyimide based on NE, MDA, BTDE and HFDE. Formulated molecular weights in the range of 1100 to 3000 were investigated. Resin flow characteristics and composite properties were determined. Composite mechanical properties were determined at room temperature and 600° F. Composite weight loss and mechanical properties retention as a function of exposure time at 600° F were also determined.

EXPERIMENTAL PROCEDURE

Monomer Preparation and Monomeric Reactant Solutions

The monomers used in this study are shown in Table I. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and 3,3',4,4'-benzophenone dianhydride (BTDA) used to prepare the dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE) were obtained from commercial sources. The 4,4'-(hexafluoroisopropylidene)-bis(phthalic anhydride) (HFDA) used to prepare the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) (HFDE) was isolated from commercially available DuPont NR 150B₂ polyimide resin solution by treatment with 10 percent excess alcoholic sodium hydroxide and heating the solution to 140° F (60° C) for a minimum of twenty minutes. The tetrasodium salt precipitate of tetra-acid (HFA) was collected by suction filtration, washed with alcohol, air dried and dissolved in water. Addition of the water solution to excess 15 percent hydrochloric acid precipitated the HFA which was collected by suction filtration, washed with water and vacuum dried at 140° F (60° C). Treatment with refluxing acetic anhydride for 2 hours converted the HFA to HFDA which precipitated in the cooled acetic anhydride solution. The HFDA was collected by suction filtration and washed with cold xylene. Concentration of the filtrate yielded three more crops of HFDA. The total yield (based on 45 percent solids of NR 150B₂ NMP solution) of isolated HFDA was 444 g (96.4 percent) of white powder, mp = 468° - 471° F (242° - 244° C) (literature mp = 489° F (254° C), ref. 5) starting from 1500 g of NR 150B₂ polyimide resin solution. A sample of the dianhydride was converted to the HFDE and used for IR, NMR, and elemental analysis, all of which agreed with the HFDE structure. The isomer mixture of HFDE melted over a range of 167° - 203° F (75° - 95° C).

The BTDE and HFDE were synthesized by refluxing a suspension of the calculated amounts of BTDA or HFDA in a calculated amount of anhydrous methanol until the solid had dissolved and then for an additional

2 hours to result in a 50 weight percent methanol solution of BTDE or HFDE. PMR reactant solutions were prepared by dissolving at room temperature the NE and MDA in the BTDE and/or HFDE solution(s) and adding anhydrous methanol to maintain 50 weight percent solutions. The stoichiometry of the reactants (NE, MDA, BTDE and/or HFDE) was governed by the desired formulated molecular weight as described in reference 3.

COMPOSITE FABRICATION

Prepreg tapes were made by drum winding and impregnating Hercules HTS graphite fiber with the various PMR monomer solutions to yield preregs containing 45.5 percent monomers and 54.5 percent fiber by weight. The prepreg tapes were air dried on the drum at room temperature for one hour and at 120⁰ F for another hour to reduce the solvent content to approximately 10 percent by weight. After this treatment, the preregs remained flexible but not tacky. The prepreg tapes were then removed from the drum, cut into 3- by 8-inch plies, and stacked unidirectionally, 8 plies thick. Prepreg that was to be cured in matched metal dies was then placed into a preforming mold and staged at 250⁰ F for three hours under an applied pressure of 0.1 psi. Composites were then molded by placing the staged prepreg into a matched metal die preheated to 450⁰ F. Following a dwell time of 10 minutes, 500 psi pressure was applied and the temperature was increased to 600⁰ F at a rate of 10⁰ F/minute. Pressure and temperature were maintained for 60 minutes. Vacuum bag press cured composites were prepared by wrapping eight plies of dried prepreg with a porous Teflon coated glass fabric and then placing three plies of bleeder cloth (style 181 E glass fabric) on each side. The bagging material was 5 mil Kapton sealed with RTV 106 sealant. The composites were fabricated by applying 15 inches of vacuum and heating at 5⁰ F/minute from room temperature to 600⁰ F. At 490⁰ F, 200 psi was applied. After reaching 600⁰ F, 200 psi was maintained for 60 minutes.

Prepreg tape was also made from DuPont's NR 150A₂ resin and HTS graphite fiber using the drum winding technique. The prepreg was dried for 2 hours at a temperature of 120° F on the drum, removed and then placed into an oven at 300° F for 20 minutes. The prepreg was then cut, stacked and bagged in a manner similar to that previously described for the PMR prepreg. The NR 150A₂ prepreg was then cured according to a cure procedure recommended by DuPont.

After curing, all composites were post-cured for 16 hours by placing them into an oven at 400° F and raising the temperature to 600° F at a rate of 4°/minute.

Resin flow was measured by determining the weight of the resin flash after curing.

COMPOSITE TESTING

Prior to specimen preparation all laminates were inspected using the ultrasonic C scan technique (ref. 6). Flexural strength tests were performed using a 3 point loading fixture with a fixed span of 2 inches. The thicknesses of the laminates ranged from 0.070 inch to 0.085 inch. The resultant span/depth ratio used ranged from 24 to 29. The rate of center loading for flexural testing was 0.05 inch/min. Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5. Elevated temperature tests were performed in an environmental heating chamber. For the flexural and shear tests the load was applied after a 15 minute soak at the test temperature. Forced convection air ovens were used for the long-term isothermal exposure at 600° F. Composite weight measurements were made throughout the exposure time period. The air change rate was 100 cubic centimeters per minute.

The properties data presented are averages of 3 or more tests at each condition. Fiber content was determined for all laminates and ranged from 53.6 to 63.5 volume percent. For flexural tests all results were normalized to 55 volume percent fiber.

RESULTS AND DISCUSSION

The monomer reactant stoichiometries used for complete substitution of HFDE for BTDE are given in Table II. The number of moles of monomeric reactants in each of the PMR solutions listed in Table II was governed by the following ratio:

$$n:(n+1):2$$

where n , $(n+1)$ and 2 are the number of moles of HFDE, MDA, and NE, respectively. The formulated molecular weight (FMW) given in Table II is considered to be the average molecular weight of the imidized prepolymer that could have been formed if imide prepolymer had been formed and terminated by the norbornene reactive end-capper. Also listed in Table II is the percent alicyclic content of each FMW.

Figure 1 shows the variation in composite weight loss as function of FMW for HFDE-PMR/HTS graphite fiber composites after exposure in air for 600 hours at 600° F. Composite weight loss ranged from 7 percent for the lowest FMW to 2 percent for the highest FMW. The increase in thermo-oxidative stability (TOS) with increasing FMW can be attributed either to the decrease in alicyclic content from 16.87 to 6.13 percent as FMW increased from 1100 to 3000 (shown in Table II) or to the increase in imide ring content as the alicyclic content decreased. All of the HFDE-PMR/HTS graphite fiber composites exhibited lower composite weight loss than the most thermally stable BTDE-PMR/HTS graphite fiber composites reported in reference 1. The BTDE-PMR/HTS composites containing 12.4 percent alicyclic content in the matrix exhibited 9.5 percent composite weight loss after 600 hours exposure in air at 600° F.

The major difference between the HFDE-PMR and BTDE-PMR matrix resins resides in the chemical nature of the group which connects the two phthalic acid monoesters present in the diesters. The HFDE contains a hexafluoroisopropylidene connecting group whereas the BTDE contains a carbonyl connecting group. Therefore, it can be concluded that the presence of the hexafluoroisopropylidene group is responsible for the improved TOS of the HFDE-PMR graphite fiber composites.

The effect of FMW on percent resin flow for HFDE-PMR matrix resins is shown in figure 2. It can be seen that resin flow increased significantly (from 13 to 35 percent) as the FMW decreased from 3000 to 1100. These results are in agreement with the findings reported in reference 3 for BTDE-PMR matrix resins. The resin flow of the BTDE-PMR matrix resin ranged from 3 to 20 percent as FMW decreased from 1500 to 1000. The higher flow characteristics of the HFDE-PMR matrix resins extends the range of FMW's which can be easily processed using the PMR approach.

The HFDE-PMR/HTS graphite fiber composite flexural strength and modulus as a function of FMW are shown in figures 3 and 4, respectively. Results are shown for specimens tested at room temperature and 600° F after short-time (15 min) and 600 hour exposure in air at 600° F. The room temperature mechanical properties are not affected by FMW. The flexural strength values are essentially identical to those found for BTDE-PMR/HTS composites (ref. 3). The 600° F short-time results show the combined effects of cross-link density and temperature. As can be seen, after short-time exposure at 600° F the flexural strength decreases as the FMW is increased. This can be attributed to a reduced cross-link density as FMW is increased (ref. 3). After 600 hours of exposure at 600° F composites made with matrix resins having a FMW equal to or greater than 1250 exhibited excellent retention of their short-time 600° F properties. In fact, for composites made from matrix resins having a FMW equal to or greater than 1400, a post-cure appears to have occurred increasing the flexural strength to levels surpassing the initial 600° F properties.

Figure 5 shows the variation in interlaminar shear strength (ILSS) with FMW. Results are shown for tests conducted at room temperature and 600° F after short-time (15 min) and 600 hour exposure at 600° F. The room temperature ILSS varies from 12 500 psi for FMW 1100 to 14 600 psi for FMW 1550. After 600 hours exposure the HFDE composites exhibited excellent retention of their initial 600° F strength over the entire range of matrix resin FMW investigated.

The HFDE-PMR/HTS composites investigated exhibit improved TOS compared to the TOS of BTDE-PMR/HTS composites reported in previous studies (ref. 1). However, for exposure times less than 800 hours at 600⁰ F the mechanical properties of the BTDE-PMR/HTS composites are considerably higher than those obtained for HFDE-PMR/HTS composites. Figure 6 shows a comparison of 600⁰ F flexural strength as a function of exposure time at 600⁰ F for composites made with matrix resins containing either HFDE or BTDE. The value of n in the expression governing the monomer stoichiometry, for both resins, was selected as 1.67. It can be seen that the flexural strength of the composites made with BTDE are higher than those of HFDE composites for all exposure times up to 800 hours. Therefore, we hypothesized that matrix resins containing mixtures of BTDE and HFDE would result in composites possessing the best overall balance of thermo-mechanical properties and TOS. Flexural strength data for composites made with 50 mole percent of each diester are shown in figure 7. Also shown in the figure are the data from figure 6. Figure 7 shows that the composites made with the mixed diesters exhibited a substantial increase in 600⁰ F flexural strength over the first 600 hours of exposure at 600⁰ F. After 600 hours exposure to 600⁰ F, their flexural strength even slightly surpassed that of the 100 percent BTDE matrix resins composites. The observed improvement in performance of composites made with the mixed diesters serves to verify our earlier stated hypothesis.

In order to quantize the effect of diester composition on composite properties, a series of composites were fabricated with resins having the monomer stoichiometries listed in Table III. As can be seen, only the molar percentage of the diesters was varied while n was held constant at 1.67. The slight variations in the percent alicyclic content and FMW are due to the molecular weight difference between HFDE (508) and BTDE (386).

Figure 8 compares percent composite weight loss as a function of exposure time at 600⁰ F for HFDE/BTDE-PMR composites made from the

monomer solutions listed in Table III. It can be seen that after 800 hours at 600° F, composites containing 100 mole percent BTDE exhibited approximately three times as much weight loss as the composite containing 100 mole percent HFDE (16 percent against 6 percent) and nearly 50 percent more weight loss than composites containing 25 mole percent HFDE. Figure 9 illustrates the improved TOS of the composites containing HFDE. Shown in the figure are flexure specimens which have been exposed for 800 hours at 600° F in air and tested at 600° F. It can be seen that the degree of surface degradation increases as the amount of BTDE in the matrix is increased.

The effects of diester composition on composite flexural strength and modulus are shown in figures 10 and 11, respectively. The diester composition of the matrix appears to have little effect on the room temperature flexural strength. Room temperature modulus increased slightly (from 14.5×10^6 to 15.5×10^6 psi) as the BTDE content increased from 0 to 100 mole percent. The 600° F short-time results show a dramatic improvement in flexural strength as the diester composition of the matrix increased from 0 to 100 mole percent BTDE. It can be seen that there is essentially a linear relation between flexural strength and the molar percentage of BTDE present in the matrix of HFDE-PMR composites. After 800 hours exposure at 600° F, the retention of initial 600° F properties for compositions of 25 to 75 mole percent BTDE ranges from 110 to 72 percent. Figure 11 shows that as little as 25 mole percent BTDE in the matrix of HFDE-PMR composites increases the flexural modulus more than 200 percent.

Figure 12 shows the effect of the matrix diester composition on ILSS. Results are shown for tests conducted at room temperature and at 600° F after short-time and 800 hours of exposure in air at 600° F. The effects of diester composition on composite ILSS are similar to those observed on flexural strength.

We have shown that the presence of hexafluoroisopropylidene connecting groups in the backbone of addition-type PMR polyimides improves composite TOS. The Dupont NR 150 condensation type polyimide resins

also contain hexafluoroisopropylidene connecting groups and are considered to have greater TOS than other commercially available condensation type polyimides (ref. 4). Figure 13 shows a comparison of composite weight loss as a function of exposure time at 600° F for a FMW 3000 HFDE-PMR/HTS composite and a NR 150A₂/HTS composite. It can be seen that after 1000 hours at 600° F, the FMW 3000 HFDE-PMR composite exhibited 4.8 percent weight loss compared to 9.8 percent weight loss for the NR 150A₂ composite. Both composites were fabricated using a vacuum bag augmented pressure method at 200 psi. The FMW 3000 HFDE-PMR composite was void free as determined by ultrasonic C-scan inspection while the NR 150A₂ composite had a void content estimated to be in the range of 10 percent. The high porosity of NR 150A₂ can be seen in figure 14 which compares photomicrographs of cross-sections of FMW 3000 HFDE and NR 150A₂ composites. The lower TOS of the NR 150A₂ composite, compared to the FMW 3000 HFDE-PMR composite, can be attributed in part to the high porosity of the NR 150A₂ composite. If void free composites were fabricated it is expected that the NR 150A₂ composite TOS would increase.

Figure 15 shows the flexural strength of the FMW 3000 HFDE-PMR/HTS composite as a function of exposure time at 600° F. No 600° F strength comparison was made between the HFDE-PMR composite and the NR 150A₂ composite because the T_g of NR 150A₂ is reported to be 550° F. It can be seen from figure 15 that the flexural strength of high molecular weight HFDE-PMR resin composites is quite low for the first 700 hours. However, the long term post-cure effect which was mentioned earlier improved the strength considerably after 700 hours exposure at 600° F. The strength increased from 58 000 psi at 700 hours to 110 000 at 1000 hours.

In order to obtain the maximum benefits of the excellent TOS of 100 percent HFDE-PMR matrix resin composites, further investigations are being conducted to determine if higher temperature post-cures can be used to improve the HFDE-PMR matrix resin mechanical properties over the first 800 hours exposure at 600° F. Also under investigation

is the use of other non-fluorinated monomer reactants to improve thermo-mechanical properties without sacrificing TOS.

In summary, the use of HFDE or mixtures of HFDE and BTDE as the diester monomer reactant in PMR composite fabrication methodology extends the service life of graphite fiber reinforced PMR polyimides at 600° F.

CONCLUDING REMARKS

The substitution of HFDE for BTDE in PMR polyimide matrix resins significantly improves the thermo-oxidative stability of PMR polyimide/graphite fiber composites. Complete substitution of HFDE for BTDE results in composites having reduced flexural strength and modulus during 600° F exposure for times up to 800 hours. After 800 hours of exposure at 600° F, the HFDE-PMR resin composites undergo a post-cure which improves these properties to levels surpassing those exhibited by BTDE-PMR resin composites. For exposure times less than 800 hours, the 600° F properties can be improved by using a mixture of HFDE and BTDE diesters.

The improvements in composite TOS offered by the use of HFDE-PMR matrix resins must be balanced against the loss in composite thermo-mechanical properties. The use of PMR matrix resins containing a mixture of HFDE and BTDE provides a means to trade off properties to obtain PMR polyimide/graphite fiber composites with the best overall balance of TOS and thermo-mechanical properties.

The excellent resin flow characteristics of HFDE-PMR resin composites extends the range of resin formulated molecular weight which can be processed by the PMR approach. These higher formulated molecular weight HFDE-PMR resins have excellent thermo-oxidative stability and are considerably easier to process than condensation type polyimide resins containing a hexafluoroisopropylidene connecting group.

The improved thermo-oxidative stability and processability of PMR polyimide matrix resins containing HFDE enhances the "tailor making" aspect of composite fabrication by the PMR approach.

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TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

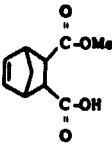
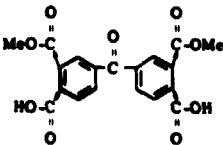
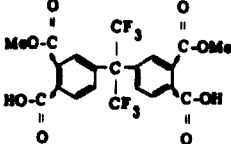
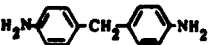
Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethyl ester of 3,3',4,4'-benzophenone-tetracarboxylic acid	BTDE
	Dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid)	HFDE
	4,4'-Methylenedianiline	MDA

TABLE II. - MONOMER STOICHIOMETRY
FOR PMR SOLUTIONS CONTAINING HFDE

Formulated molecular weight	Moles of HFDE ^a n	Percent alicyclic content
1100	1.0	16.72
1250	1.25	14.72
1400	1.50	13.14
1550	1.75	11.87
1700	2.0	10.82
3000	4.14	6.13

^aMolar ratio of HFDE/MDA/NE equals
n:(n+1):2.

**TABLE III. - MONOMER STOICHIOMETRY OF
PMR SOLUTIONS CONTAINING A MIXTURE
OF BTDE AND HFDE**

Formulated molecular weight	Moles of diester-diacid ^a		Percent alicyclic content
	BTDE n_1	HFDE $n-n_1$	
1300	1.670	0	14.15
1350	1.253	0.417	13.62
1400	.835	.835	13.14
1450	.417	1.253	12.68
1500	0	1.670	12.26

^aMolar ratio of BTDE/HFDE/MDA/NE equals
 $n_1:(n-n_1):(n+1):2$, $n = 1.67$.

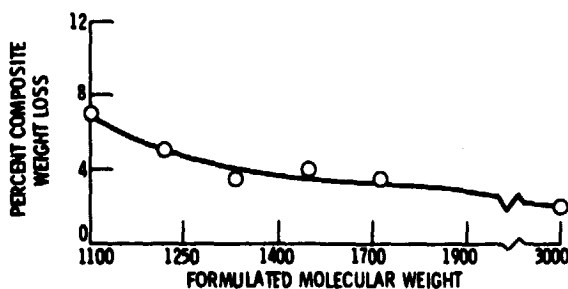


Figure 1. - Weight loss of HFDE-PMR/HTS graphite fiber composites after exposure for 600 hours at 600° F in air.

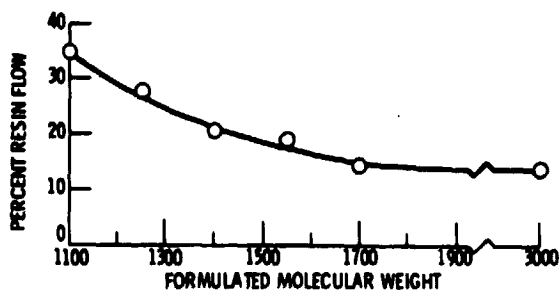


Figure 2. - Percent resin flow during cure for PMR polyimide composites containing HFDE.

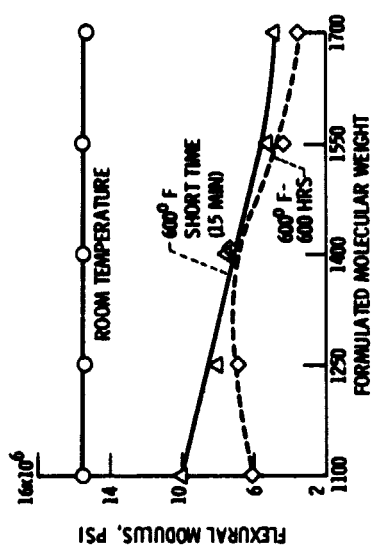


Figure 4. - Flexural modulus of HFDE-PMR/HTS graphite fiber composites. Tests conducted at room temperature and at 600° F after short-time and 600 hour exposure at 600° F in air.

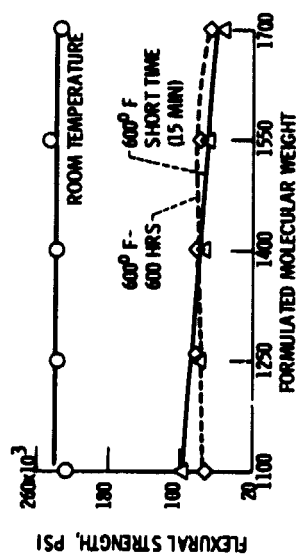


Figure 3. - Flexural strength of HFDE-PMR/HTS graphite fiber composites. Tests conducted at room temperature and at 600° F after short-time and 600 hour exposure at 600° F in air.

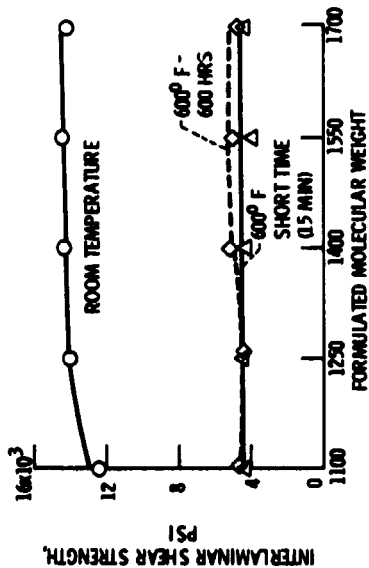


Figure 5. - Interlaminar shear strength of HFDE-PMR/HTS graphite fiber composites. Tests conducted at room temperature and at 600° F after short-time and 600 hour exposure at 600° F in air.

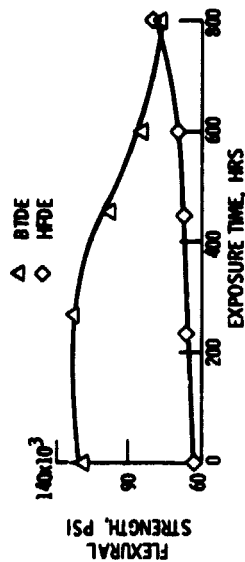


Figure 6. - Flexural strength comparison at BTDE-PMR and HFDE-PMR/HTS graphite fiber composites exposed and tested at 600° F in air.

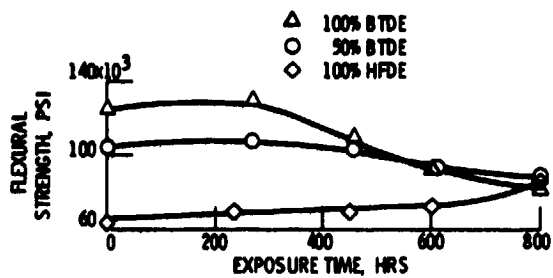


Figure 7. - Flexural strength comparison of BTDE-PMR, BTDE/HFDE-PMR and HFDE-PMR/HTS graphite fiber reinforced composites exposed and tested at 600° F in air.

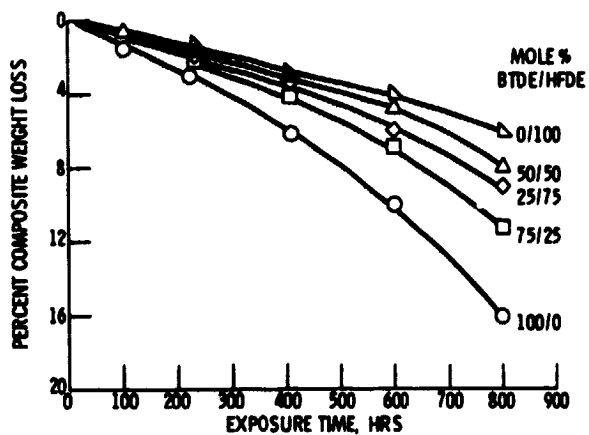
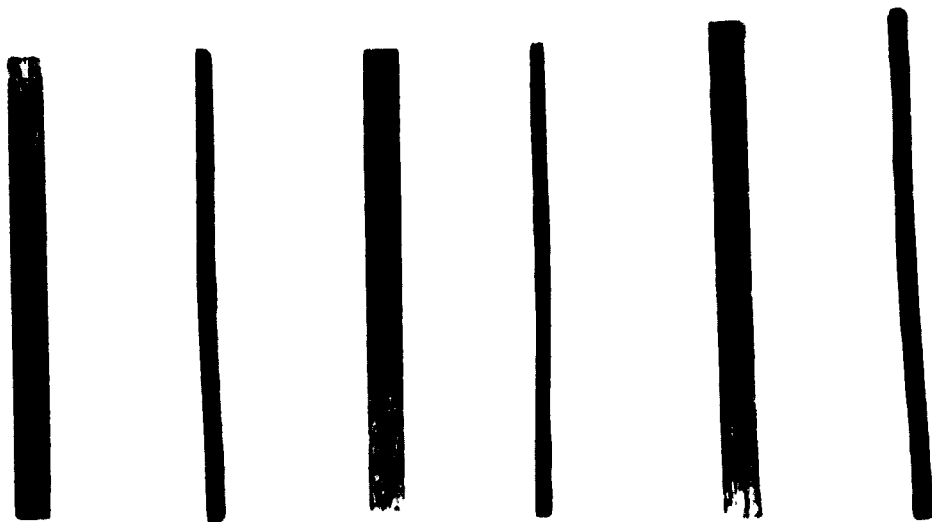


Figure 8. - Comparison of weight loss after 600° F exposure in air for PMR/HTS graphite fiber composites containing BTDE and HFDE at the molar ratios indicated.



100 MOLE PERCENT HFDE

75 MOLE PERCENT HFDE

50 MOLE PERCENT HFDE



25 MOLE PERCENT HFDE

100 MOLE PERCENT BTDE

Figure 9. - HFDE/BDDE - PMR/HTS composite flexural specimens showing the effect of diester composition on surface degradation after 800 hours exposure and testing at 600° F in air. Specimens tested at a fixed span of 2 inches. X1.

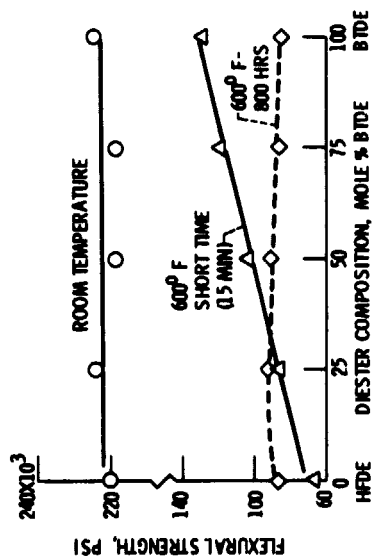


Figure 10. - Flexural strength of PMR/HTS graphite fiber composites containing HFDE and BTDE. Tests conducted at room temperature and at 600° F after short-time and 800 hour exposure at 600° F in air.

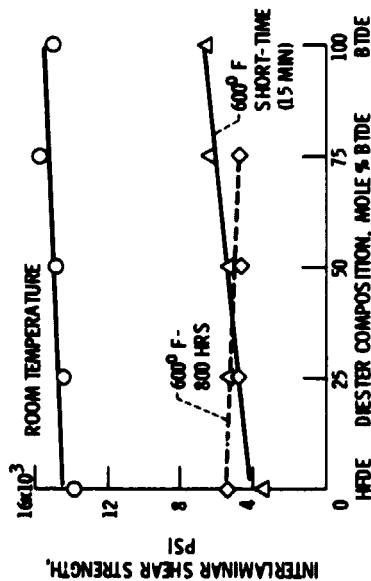


Figure 12. - Interlaminar shear strength of PMR/HTS graphite fiber composites containing HFDE and BTDE. Tests conducted at room temperature and at 600° F after short-time and 800 hour exposure at 600° F in air.

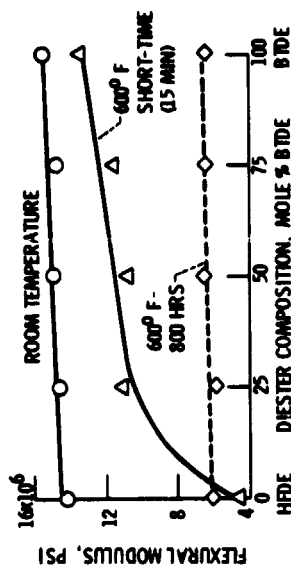


Figure 11. - Flexural modulus of PMR/HTS graphite fiber composites containing HFDE and BTDE. Tests conducted at room temperature and at 600° F after short-time and 800 hour exposure at 600° F in air.

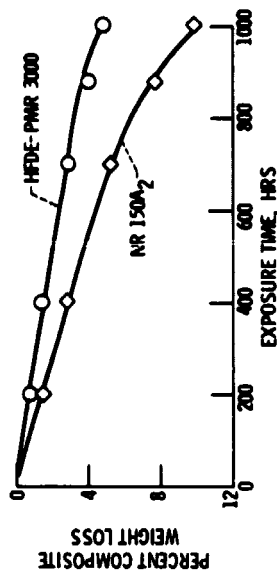
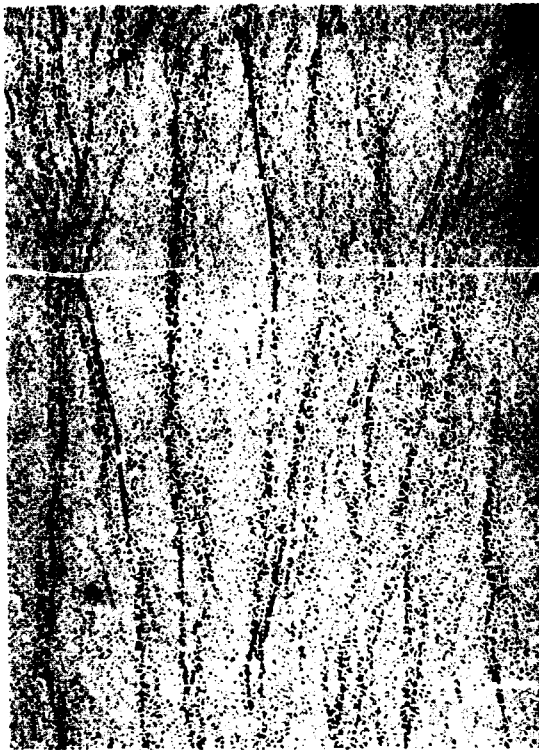
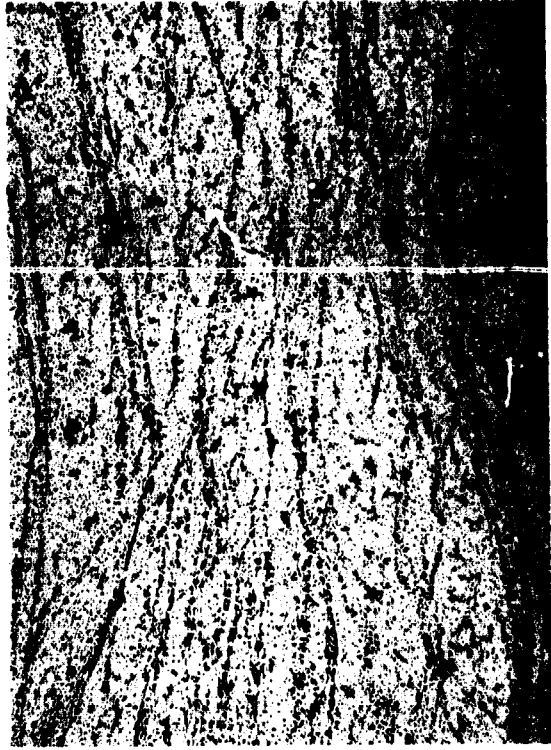


Figure 13. - Weight loss comparison of addition and condensation type polyimide/HTS graphite fiber composites after exposure at 600° F in air.



FMW 3000 PMR/HTS



NR 150 A₂/HTS

Figure 14. - Photomicrographs of addition-type FMW 3000 PMR/HTS and condensation type NR 150 A₂/HTS polyimide composites. X50.

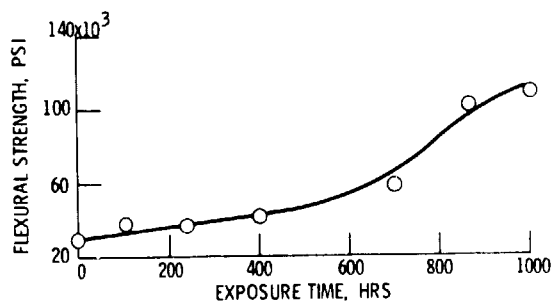


Figure 15. - Flexural strength of FMW 3000 HFDE-PMR/HTS graphite fiber composites exposed and tested at 600° F in air.